Magnetic coupling and dynamics in solid $\alpha$ and $\beta$-O$_2$. I. An ab initio theoretical approach

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This paper describes a new approach to the dynamic and magnetic properties of solid $\alpha$ and $\beta$ oxygen which is based on two theoretical developments. First, we have constructed the lattice and spin Hamiltonian for solid O$_2$ by including explicitly the interactions between the triplet ground state O$_2$ molecules as obtained mainly from recent ab initio calculations. The spin coupling parameters in this Hamiltonian, especially the Heisenberg exchange parameter $J$, are strongly dependent on the positions and orientations of the molecules. Secondly, we have developed an integrated scheme for lattice dynamics and spin wave calculations which uses this Hamiltonian. The actual mixing between the lattice modes, phonons and librations, and the magnons appears to be small; their interaction can be largely taken into account by renormalization of the coupling terms. In the lattice dynamics part of the calculation it is essential to include the Heisenberg term, since it is the extremely strong anisotropy of the coupling parameter $J$ that explains the anomalously large libron splitting in $\alpha$-O$_2$. The spin-wave calculation with the Hamiltonian averaged over the lattice vibrations yields reasonable values for the magnon frequencies with no empirical fit parameters.

I. INTRODUCTION

Solid oxygen is one of the most interesting molecular crystals because of its behavior as a magnetic material. This behavior is due to the rather unique property of the O$_2$ molecule of possessing a (triplet) electronic spin momentum in its ground state. In the condensed phases these spin momenta can be coupled in various ways which are related to the geometrical order of the molecules, and this leads to a very rich phase diagram.\(^1,2\) Most studies have been devoted to the $\alpha$ and $\beta$ phases. Under its own vapor pressure the $\alpha$ phase is stable from 0 to 23.9 K and the $\beta$ phase from 23.9 to 43.8 K, but the latter phase remains stable until above room temperature at higher pressures. Both these phases are structurally ordered. The O$_2$ molecules are arranged in layers parallel to the $a$-$b$ plane, see Fig. 1, with their axes perpendicular to this plane. In the rhombohedral $\beta$ phase the order within the layers is close packed hexagonal, whereas in the monoclinic $\alpha$ phase the hexagons are slightly distorted. The $\alpha$-O$_2$ solid is a two-sublattice antiferromagnet, with the spins preferentially aligned parallel to the $+b$ axis. For $\beta$-O$_2$, short range antiferromagnetic order in three sublattices with 120° angles between the spins has been deduced from experiment. It is now generally believed that the structural distortion from the geometrically most favorable close packed $\beta$ phase to the $\alpha$ phase is driven by the magnetic (Heisenberg exchange) interaction between the molecules; the antiferromagnetic order in $\alpha$-O$_2$ leads to a lower magnetic (and total) energy than that in $\beta$-O$_2$.

Many more experimental data of various kinds, optical, magnetic, and thermodynamic, have been collected on $\alpha$- and $\beta$-oxygen.\(^1-7\) The theoretical approaches which have been made in order to interpret these data clearly fall into two categories. On the one hand, one has tried to understand the elastic and optical properties via standard harmonic lattice dynamics calculations.\(^8-10\) These calculations have ignored the open shell (triplet) character of the O$_2$ molecules and they have used a standard empirical atom–atom potential which is common between closed shell molecules. A typical feature that cannot be explained by such calculations, despite the possible variation of the parameters in the empirical potential, is the splitting of the optical ($q = 0$) librion mode which occurs at the phase transition from $\beta$-O$_2$ to $\alpha$-O$_2$. Given the small structural distortion of $\alpha$-O$_2$ with respect to $\beta$-O$_2$, this splitting is very large indeed (more than 30 cm$^{-1}$). Since the lattice dynamics calculations all gave a splitting of 10 cm$^{-1}$ at most, it was usually assumed that the higher frequency peak in the Raman spectrum of $\alpha$-O$_2$ corresponds with a two phonon/libron or librion–magnon transition. Recent experimental data\(^11-10\) seem to invalidate this assumption, however, and so the anomalously large splitting has still to be explained.

On the other hand, one has interpreted the magnetic data by means of spin-wave calculations based on a pure spin Hamiltonian.\(^3,4,11,12\) The following form is generally accept- ed for this Hamiltonian in $\alpha$-O$_2$:

$$H_{\text{spin}} = -2 \sum_{P \neq P'} J_{PP'} S_P \cdot S_{P'} + \sum_P (AS_{P}^{2} + BS_{P}^{2}).$$

The first term is the usual Heisenberg exchange term, which couples the spins $S_P$ and $S_{P'}$ on the lattice sites $P$ and $P'$. Since this term, which is isotropic in the spin, was not sufficient to explain the experimental data, one has simply added two single particle spin terms with the anisotropy parameters $A$ and $B$. The first of these terms, with $A > 0$, keeps the spins preferentially directed perpendicular to the molecular axes (i.e., to the $e^*$ axis which we take to be the $x$ axis). The second single particle term with $B > 0$ determines the preferential spin axis within the $a$–$b$ plane, i.e., the $b$ axis (which we take as the $z$ axis). The parameters $J_{PP'}$, $A$, and $B$, are...
regarded as empirical constants. They must be chosen such that the properties calculated from this Hamiltonian via mean-field or spin-wave models agree with the measured data. The exchange coupling constant $J_{PP}$ is only included between nearest and next-nearest neighbors within the $a$-$b$ plane and between nearest neighbors in adjacent planes; it is negative for all these pairs, i.e., the coupling is antiferromagnetic. In a few papers this Hamiltonian has also been applied to $\beta$-$O_2$ setting the in-plane anisotropy parameter $B$ equal to zero.

It will be clear from this description that the spin Hamiltonian (1) is a purely phenomenological one; it has not been derived from the properties of the interacting molecules. Still, there is some justification for each of its terms. The form of the Heisenberg term can be derived from first principles.\textsuperscript{13,14} The term $AS^z_2$ is believed to correspond to the intramolecular spin-orbit and spin-spin coupling,\textsuperscript{15} which would indeed yield such a term for every $O_2$ molecule if the molecular axes are placed parallel to the $x$ axis (the crystal $c^*$ axis). The free molecule value of the constant $A$ equals 5.712 K. The term $BS^z_2$ is believed to originate from the magnetic dipole–dipole interactions between the triplet spins of the $O_2$ molecules. The only justification for this term is that it leads to the same preferred magnetization direction (parallel to the $z$ axis or crystal $b$ axis) as a classical dipole–dipole interaction model, with the correct order of magnitude for the anisotropy parameter $B$.

The treatments based on the phenomenological spin Hamiltonian (1) are unsatisfactory, however, in that they have led to very different sets of parameters $J_{PP}$, $A$, and $B$ when the results were fitted to different experimental data. This is most clearly demonstrated in DeFotis’s review\textsuperscript{3} which contains parameters from various papers that vary by an order of magnitude. Although it is argued in a recent paper\textsuperscript{4} that the results are becoming more consistent if the appropriate corrections are made, it is typical that even there the empirical values of $A$ and $B$ are only half the “free molecule” values. In view of the small distortions of the molecular charge distributions\textsuperscript{16} by the weak van der Waals interactions in solid $O_2$, this is hard to explain (at least at low pressures). Moreover, we find it very unsatisfactory that the Hamiltonian (1) represents the magnetic dipole–dipole interactions between pairs of molecules $P$ and $P'$ by a single particle term.

From the stability considerations on the $\alpha$-$\beta$ phase transition it is obvious that structural changes and the magnetic coupling are strongly related in solid $O_2$. In some recent theoretical treatments of this phase transition\textsuperscript{9,10,17} one has included the dependence of the Heisenberg coupling parameter $J_{PP}$ on the distance $R_{PP}$ between the molecules, as derived from temperature and pressure dependent measurements.\textsuperscript{18,19} From \textit{ab initio} electronic structure calculations in our institute\textsuperscript{20,21} the same distance dependence has been obtained, but it has been found, moreover, that $J_{PP}$ depends very sensitively on the orientations of the molecules $P$ and $P'$. This being the case, the Heisenberg spin operator depends strongly on the displacements of the molecules in the lattice, both translational and orientational, and it is no longer justified \textit{a priori} to perform separate lattice dynamics and spin-wave calculations.

In a recent communication\textsuperscript{22} it was announced that we have developed an integrated lattice dynamics and spin-wave scheme which includes the coupling between phonons, librons, and magnons. This scheme starts from a Hamiltonian...
nian which is based on first principles. The spin-independent potential \( V_{pp} \) in this Hamiltonian and the geometry dependent Heisenberg coupling parameters \( J_{pp} \) have been obtained from quantum chemical \textit{ab initio} calculations. Also the geometry dependence of the coupling parameter \( A \) in Eq. (1) is explicitly included and the last term from Eq. (1) is replaced by the exact two-particle operator for the magnetic dipole–dipole interactions. The results of this approach are mostly in good agreement with experimental data, without any fitting of empirical parameters. However, this approach does not only provide, from first principles, results which can be compared with measurements, it also offers a physical explanation of some of the observed phenomena. In the present paper, this new approach is more fully presented and its results are discussed.

II. THEORY

A. The spin-dependent intermolecular potential and the Hamiltonian of solid O\(_2\)

The interactions between ground state \( ^3\Sigma^- \) O\(_2\) molecules depend on the coupling between their triplet electronic spin momenta. So, for example, if we take a pair of O\(_2\) molecules the two triplets can couple to a singlet, a triplet, or a quintet. Neglecting in first instance the spin–orbit coupling and the magnetic dipole interactions, each of these three dimer spin states leads to its own potential surface. It is in fact by calculating the three potential surfaces for an O\(_2–O_2\) dimer that the leading terms in the spin-dependent \( ^3\Sigma^- \)–O\(_2\) potential have been obtained.\(^{20,21}\) The exchange interactions, in particular, cause the energy separation between the three surfaces. It has been found from the \textit{ab initio} calculations that the three \( ^3\Sigma^-–O_2\) potential surfaces can be accurately represented by the following expression

\[
V_{pp} (\omega_p, \omega_p, \omega_p) = 2 J_{pp} (\omega_p, \omega_p, \omega_p) S_p \cdot S_p.
\]

(2)

The first, spin-independent, potential is the (multiplicity weighted) average of the \( S = 0, 1, \) and 2 potential surfaces. The second, Heisenberg, term accurately describes the splitting between the three surfaces. The latter result implies that the quintet–singlet splitting is almost exactly twice the triplet–singlet splitting, for any geometry of the O\(_2–O_2\) dimer in the van der Waals distance range. The geometry of the dimer is characterized in an arbitrary system of axes by the vector \( r_{pp'} = r_{pp'} - r_p \) with \( r_p \) and \( r_{pp'} \) describing the center of mass positions of the molecules \( P \) and \( P' \), and by the polar angles \( \omega_p = (\theta_p, \phi_p) \) and \( \omega_{p'} = (\theta_{p'}, \phi_{p'}) \) describing the orientations of both molecules.

Thus it has been found that the Heisenberg coupling parameter \( J_{pp} \) depends on the positions and orientations of the molecules \( P \) and \( P' \), just as the spin-independent potential \( V_{pp} \). Actually, the anisotropy of the parameter \( J_{pp} \) is much stronger even than the anisotropy of \( V_{pp} \). The orientational dependence of both these quantities can be explicitly expressed by the expansions:

\[
J_{pp} (\omega_p, \omega_p, \omega_p) = (4\pi)^{3/2} \sum_{L_{pp'} L_{pp'} L} J_{L_{pp'} L_{pp'} L} (r_{pp'}, \omega_p, \omega_p),
\]

(3)

in the complete orthonormal set of angular functions:

\[
A_{L_{pp'} L_{pp'} L} (\omega_p, \omega_p, \omega_p) = \sum_{M_A M_B M} \begin{pmatrix} L_A & L_B & L \\ M_A & M_B & M \end{pmatrix} \times Y_{M_A}^{(J_{pp})} (\omega_p) Y_{M_B}^{(J_{pp})} (\omega_p) Y_{M}^{(J_{pp})} (\omega_p),
\]

(4)

with \( \hat{r}_{pp'} \) denoting the polar angles \( (\Theta_{pp'}, \Phi_{pp'}) \) of the vector \( r_{pp'} \). The symbol in large brackets is a 3-j coefficient and \( Y_m^{(\alpha, \beta)} (\theta, \phi) \) are normalized spherical harmonics.\(^{23}\) All the physical information is contained in the expansion coefficients. The coefficients \( V_{L_{pp'} L_{pp'} L} (r_{pp'}) \) contain long range \( r_{pp'} \) contributions from electrostatic multipole interactions \((n = 5, 7, 9, \text{etc.})\) and from dispersion interactions \((n = 6, 8, 10, \text{etc.})\), as well as short range (overlap) contributions from exchange and charge penetration effects which depend exponentially on \( r_{pp'} \). The Heisenberg expansion coefficients \( J_{L_{pp'} L_{pp'} L} (r_{pp'}) \) are exponential functions of \( r_{pp'} \) as they are generated purely by exchange effects. Most of the contributions to the coefficients \( V_{L_{pp'} L_{pp'} L} (r_{pp'}) \) and the complete coefficients \( J_{L_{pp'} L_{pp'} L} (r_{pp'}) \) have been explicitly calculated by \textit{ab initio} quantum chemical methods.\(^{21}\) Therefore, we can directly use Eqs. (3) and (4) as an analytical spin-dependent \( ^3\Sigma^-–O_2\) potential. The observation that the Heisenberg parameter \( J_{pp} \) is more strongly anisotropic than the spin-independent potential \( V_{pp} \) is reflected by the slower convergence of its spherical expansion (3). It has been found\(^{21}\) in particular that the coefficient \( J_{L_{pp'} L_{pp'} L} \) with \( L_A = L_B = 4 \) and \( L = 8 \) is even larger than the isotropic \( L_A = L_B = L = 0 \) contribution for most distances of interest. This is related to the nodal character of the antibonding \( \pi \) orbitals in the O\(_2\) molecules which contain the unpaired electrons that couple to the \( ^3\Sigma^- \) ground states.

If we wish to write down the complete spin-dependent potential for a pair of interacting O\(_2\) molecules we have to add the effects of spin–orbit and magnetic dipole (spin–spin) coupling. It is well known\(^{15}\) that in the free O\(_2\) molecule the effects of spin–orbit and spin–spin coupling in the electronic ground state can be represented by the following operator:

\[
\sum_{m_m} A_{m_m} (\omega) S_m S_m^* (1^{(m)} 1^{(m')} m m' - m m').
\]

(5)

where \( \omega = (\theta, \phi) \) describes the orientation of the molecular axis, \( A_m (\omega) \) is a second rank tensor:

\[
A_m (\omega) = A \sqrt{30} C_m^{(2)} (\omega),
\]

(6)

\( C_m^{(2)} (\theta, \phi) \) is a Racah spherical harmonic\(^{23}\) and \( S_m \) with \( m = -1, 0, 1 \) are the spherical harmonics of the spin operator \( S \). Equation (5) expresses the coupling between the direction of the triplet spin-momentum \( S \) and the direction of the molecular axis in a general coordinate frame. For a free O\(_2\) molecule the coupling constant \( A \) equals 3.96 cm\(^{-1}\) = 5.712 K, but also in van der Waals complexes of O\(_2\) with
rare gas atoms very nearly the same value of $A$ has been found. So, we can include the intramolecular spin–orbit and spin–spin interactions by writing a single-particle operator of the form (5) for every O$_2$ molecule $P$. In addition we include the magnetic dipole–dipole (spin–spin) interactions between the triplet magnetic momenta $g_e \mu_B S_p$ and $g_e \mu_B S_{p'}$. Of different molecules $P$ and $P'$, with $g_e = 2.0023$ and $\mu_B$ being the Bohr magneton. These interactions can be written as follows:

$$\sum_{m, m'} T_{-m-m'}(r_{pp'}) S_{m_p} S_{m_{p'}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right)$$

(7)

with the magnetic dipole–dipole interaction tensor:

$$T_m(r_{pp'}) = -\frac{1}{30} g_e^2 \mu_B^2 r_{pp'}^3 \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right)$$

(8)

and the spin momenta $S_p$ and $S_{p'}$ expressed in spherical components.\(^{23}\)

Combining all the spin-dependent interactions we can write the complete spin Hamiltonian for solid O$_2$:

$$H_{\text{spin}} = -2 \sum_{p < p'} J(r_{pp'}, \omega_p, \omega_{p'}) S_p \cdot S_{p'} + \sum_p \left( \sum_{m, m'} A_{-m-m'}(\omega_p) S_{m_p} S_{m_{p'}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right) + \sum_{p < p'} \sum_{m, m'} T_{-m-m'}(r_{pp'}) S_{m_p} S_{m_{p'}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right) \right)$$

(9)

This Hamiltonian has been derived from first principles and it applies to any phase of solid O$_2$ (and to the liquid). It has three terms just as the phenomenological spin Hamiltonian (1). All the spin coupling parameters in this new Hamiltonian (9) are dependent on the molecular positions $r_p$ and orientations $\omega_p$, however, and the last single-particle anisotropic spin term in Eq. (1) has been replaced by a two-body operator.

The dependence of the spin Hamiltonian on the molecular positions and orientations, which is explicitly given by Eqs. (3)–(8), will couple the spin waves (magnons) to the lattice vibrations (phonons and librons). In order to calculate this coupling we need the complete lattice and spin Hamiltonian. This Hamiltonian reads as follows:

$$H = H_0 + H_{\text{spin}}$$

(10)

with $H_{\text{spin}}$ given by Eq. (9) and

$$H_0 = \sum_P T(r_p) + \sum_P L(\omega_p) + \sum_{p < p'} V(r_{pp'}, \omega_p, \omega_{p'})$$

(11)

The latter Hamiltonian is ordinarily used in lattice dynamics calculations. It contains the kinetic energy terms for the translational and librational motions of the molecules:

$$T(r_p) = -\frac{\hbar^2}{2M} \nabla^2 (r_p)$$

$$L(\omega_p) = -\frac{\hbar^2}{2I} I^2 (\omega_p)$$

(12)

with $M$ and $I$ being the molecular mass and moment of inertia, respectively, and $V(r_p)$ and $I(\omega_p)$ being the gradient and angular momentum operators. The spin-independent potential $V$ has already been specified in Eqs. (2) and (3).

One more preparatory job has still to be performed before we can actually make lattice dynamics and spin-wave calculations with the Hamiltonian (10). All the two-body terms in Eqs. (9) and (11) contain the vector $r_{pp'}$ as a variable, i.e., the difference vector of the instantaneous position vectors $r_p$ and $r_{p'}$. In lattice dynamics one has to know the potential explicitly as a function of the molecular displacements $u_p = r_p - R_p$ from their equilibrium positions $R_p$. This problem can be solved by expanding all functions depending on $r_{pp'}$ as a double Taylor series in $u_p$ and $u_{p'}$, including harmonic (second order) as well as anharmonic (higher order) terms. In practice this is not simple but the procedure has been completely described in Ref. 26. Alternative procedures can be thought of, in principle, as long as they yield the potential explicitly as a function of $u_p$ and $u_{p'}$.

So, from here on we will assume that all the terms in the potential that depend on $r_{pp'}$ are now dependent on $u_p$ and $u_{p'}$. If we had applied the usual formalism for lattice dynamics calculations, i.e., the harmonic or quasiharmonic method, then a similar expansion for the angular displacements should have been made. By using a new method developed in our institute, 26–29 which is valid also for large amplitude librations, we avoid this problem.

We end this section by writing the different terms in the potential in a form that clearly shows on which variables they depend and, moreover, is convenient for use in the next section:

$$V_{pp'} = V(u_p, \omega_p; u_{p'}, \omega_{p'}) = V(r_{pp'}, \omega_p, \omega_{p'})$$

$$W_{pp'} = W(u_p, \omega_p; S_p; u_{p'}, \omega_{p'}; S_{p'})$$

$$= -2J(r_{pp'}, \omega_p, \omega_{p'}) S_p \cdot S_{p'}$$

$$X_p = X(\omega_p; S_p) = \sum_{m, m'} A_{-m-m'}(\omega_p) S_{m_p} S_{m_{p'}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right)$$

$$Y_{pp'} = Y(u_p, S_p; u_{p'}, S_{p'})$$

$$= \sum_{m, m'} T_{-m-m'}(r_{pp'}) S_{m_p} S_{m_{p'}} \left( \begin{array}{ccc} 1 & 1 & 2 \\ m & m' & -m - m' \end{array} \right)$$

(13)

B. Integrated lattice dynamics and spin-wave formalism

Both the common spin-wave formalism and the lattice dynamics methods developed in our institute, 26–29 for large amplitude librions and for librion–phonon coupling use the time-dependent Hartree (TDH) method or random phase approximation (RPA). Therefore, it seemed convenient to use the same method for an integrated formalism that includes magnon–phonon and magnon–libron coupling as well. We start with the mean field (MF) approximation and, in analogy with the phonon–libron method, 26 we write sepa-
rate MF single particle Hamiltonians for the translational vibrations;
\[
H^T_p(\omega_p) = T(\omega_p) + \sum_{p' \neq p} \langle V(u_p, \omega_p; u_{p'}, \omega_{p'}) \rangle L_p^T_{p', \omega_p} \\
+ \sum_{p' \neq p} \langle W(u_p, \omega_p; S_p; u_{p'}, \omega_{p'}; S_{p'}) \rangle T_p^S_{p', \omega_p} \\
+ \sum_{p' \neq p} \langle Y(u_p, S_p; u_{p'}, \omega_{p'}; S_{p'}) \rangle S_p^T_{p', \omega_p} \tag{14}
\]
for the librations:
\[
H^L_p(\omega_p) = L(\omega_p) + \sum_{p' \neq p} \langle V(u_p, \omega_p; u_{p'}, \omega_{p'}) \rangle L_p^L_{p', \omega_p} \\
+ \sum_{p' \neq p} \langle W(u_p, \omega_p; S_p; u_{p'}, \omega_{p'}; S_{p'}) \rangle T_p^S_{p', \omega_p} \\
+ \langle X(\omega_p, S_p) \rangle S_p \tag{15}
\]
and for the spins:
\[
H^S_p(S_p) = \sum_{p' \neq p} \langle W(u_p, \omega_p; S_p; u_{p'}, \omega_{p'}; S_{p'}) \rangle T_p^S_{p', \omega_p} \\
+ \langle X(\omega_p, S_p) \rangle L_p \\
+ \sum_{p' \neq p} \langle Y(u_p, S_p; u_{p'}, \omega_{p'}; S_{p'}) \rangle T_p^T_{p', \omega_p} \tag{16}
\]
The different potential terms are defined in Eq. (13). The subscripts and superscripts on the angle brackets denote MF states.

For the single-particle Hamiltonians, we first apply the translational symmetry by writing excitation operators:
\[
e^i_{p,k}(q) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i q \mathbf{R}} a^{(K)i}_p(\mathbf{R}, \mathbf{i} k) \tag{19}
\]
where \( q \) is a vector in the first Brillouin zone, \( \mathbf{R} \) a primitive translation vector of the crystal, \( I \) labels the different sublattices, and \( N \) is the number of unit cells. A specific molecule \( P \) in the crystal is thus labeled by the position vector \( \mathbf{R} \) of the origin of its unit cell and by its sublattice index \( I \). Substituting the operators (19) and their Hermitian conjugates into the Hamiltonian (18), the latter becomes a direct sum of the single-particle coupling terms (\( K = K', P = P' \)) which have been neglected at the MF level are thus reincorporated into the formalism. The expressions for the coupling coefficients \( A^{K,K'}_{pp'}(i_k, j_{k'}) \) and \( B^{K,K'}_{pp'}(i_k, j_{k'}) \) can be obtained by equating the matrix elements of the Hamiltonian (18) to those of the exact Hamiltonian (10) in the basis (17).

In order to be able to diagonalize the Hamiltonian (18) for the infinite crystal, we first apply the translational symmetry by writing excitation operators:
\[
e^i_{p,k}(q) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i q \mathbf{R}} a^{(K)i}_p(\mathbf{R}, \mathbf{i} k) \tag{19}
\]
where \( q \) is a vector in the first Brillouin zone, \( \mathbf{R} \) a primitive translation vector of the crystal, \( I \) labels the different sublattices, and \( N \) is the number of unit cells. A specific molecule \( P \) in the crystal is thus labeled by the position vector \( \mathbf{R} \) of the origin of its unit cell and by its sublattice index \( I \). Substituting the operators (19) and their Hermitian conjugates into the Hamiltonian (18), the latter becomes a direct sum of independent Hamiltonians for every wave vector \( q \). The exact excitation operators of the crystal \( C_\lambda(q)^+ \) must satisfy the following equation of motion:
\[
[H, C_\lambda(q)^+] = \hbar \omega_\lambda(\mathbf{q}) C_\lambda(q)^+ \tag{20}
\]
by expressing these operators as
\[
C_\lambda(q)^+ = \sum_{k,i,\lambda} \left[ \chi_{\lambda,i}^{(K)} a_{i,k}^{(K)}(q)^+ + \chi_{\lambda,i}^{(K)} a_{i,k}^{(K)}(q)^+ \right] \tag{21}
\]
Equation (20) with the Hamiltonian (18) will be exactly solved, if the expansion coefficients \( \chi_{\lambda,i}^{(K)}, \chi_{\lambda,i}^{(K)} \) are the eigenvectors of the following matrix:

\[ H_{\lambda,i}(q) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{-i q \mathbf{R}} H(\mathbf{R}, \mathbf{i} k) \tag{22} \]

The sub-blocks of this matrix which are labeled by $K = T$, $K = L$, and $K = S$ for phonons, librons and magnons, respectively, are defined as follows, with the operators written as in Eq. (13): 

\[
\begin{pmatrix}
E^{(L)} + \Phi^{(LL)} & \Phi^{(LT)} & \Phi^{(LS)} & -\Phi^{(LL)} & -\Phi^{(LT)} & -\Phi^{(LS)} \\
\Phi^{(LT)\dagger} & E^{(T)} + \Phi^{(TT)} & \Phi^{(TS)} & -\Phi^{(LT)\dagger} & -\Phi^{(TT)} & -\Phi^{(TS)} \\
\Phi^{(LS)\dagger} & \Phi^{(TS)\dagger} & E^{(S)} + \Phi^{(SS)} & -\Phi^{(LS)\dagger} & -\Phi^{(TS)\dagger} & -\Phi^{(SS)} \\
\Phi^{(LL)} & \Phi^{(LT)} & \Phi^{(LS)} & -\Phi^{(LL)} & -\Phi^{(LT)} & -\Phi^{(LS)} \\
\Phi^{(LT)} & \Phi^{(TT)} & \Phi^{(LS)} & -\Phi^{(LT)} & -E^{(T)} - \Phi^{(TT)} & -\Phi^{(LS)} \\
\Phi^{(LS)\dagger} & \Phi^{(TT)\dagger} & \Phi^{(SS)} & -\Phi^{(LS)\dagger} & -\Phi^{(TT)\dagger} & -\Phi^{(SS)} 
\end{pmatrix}
\]  

(22)

Here $\Delta e^K_{ik}$ is a MF excitation energy to the state $i_K$ of the MF Hamiltonian. Single-molecule ground states have been omitted from the notation of the matrix elements for brevity. The eigenvalues of the matrix (22) are the excitation energies of the crystal $\hbar\omega_A(q)$, and the corresponding deexcitation energies, which in principle correspond to mixed phonon-libron-magnon $(K = L,T,S)$ excitations.

C. Separate lattice dynamics and spin-wave treatments

As shown by the results (Sec. III) of applying Sec. II B, the actual mixing between phonons and librons, on the one hand, and magnons, on the other, is small in the case of $\alpha$ and $\beta$ oxygen, except for some isolated points in the Brillouin zone. This is caused by the smallness of the $TS$ and $LS$ coupling blocks in the matrix (22). So it is possible to describe most of the properties of these systems in good approximation by separate lattice dynamics and spin-wave treatments. These treatments are still essentially different from the earlier separate treatments, however. In principle, we base each formalism on the complete lattice and spin Hamiltonian (9)–(11). The mean-field calculations for the translational vibrations, for the librations and for the spins are made as in Sec. II B, Eqs. (14)–(16), and the separation only implies that we solve the RPA problems separately for the phonons and librons and for the spin waves. Although from the point of view of the calculations this is not a great simplification, conceptually the separation is advantageous. We treat the lattice vibrations in the averaged field of the spins and the spin waves in the average field of the vibrating molecules. Or, in the actual calculations, those terms in the complete Hamiltonian (9)–(11) that depend both on the lattice vibrations and the spins are averaged over the spins when calculating
the lattice modes and averaged over the molecular vibrations when calculating the spin waves. This thermodynamic averaging, sometimes called renormalization, is performed in the sense of MF theory. Moreover, the separation allows practical simplifications because some of the renormalized terms are insignificant.

Let us now be specific about the essential differences between our separated treatment and the earlier calculations. In the older lattice dynamics calculations, the Hamiltonian $H_0$, given by Eq. (11), has been taken into account. In our lattice dynamics calculations we have included, moreover, the first two terms from the spin Hamiltonian (9), averaged over the spin states from a MF calculation. Especially the Heisenberg term with the spin factor $(S_{p} \cdot S_{p'})/S_{p}'$ turns out to be crucial, see Sec. III, because of the extremely strong dependence of the coupling parameter $J$ on the molecular orientations $\omega_p$. The third term in Eq. (9) appears to be insignificant for the lattice dynamics calculations, and also the effects of the second term are of minor importance.

In our spin-wave calculations we have used the spin Hamiltonian (9) with coupling parameters $\langle J(r_{pp'}, \omega_{pp'}, \omega_{pp'}) \rangle$, $\langle A_m(\omega_{pp'}) \rangle$, and $\langle T_m(r_{pp'}) \rangle$ averaged over the vibrational wave functions of the molecules. When we identify these averaged parameters with the spin-coupling constants in Eq. (1), our spin Hamiltonian (9) becomes conceptually similar to the phenomenological one in Eq. (1). Two essential differences persist, however. Our coupling parameters have been obtained from ab initio calculations, not by fitting the experimental data. Secondly, the ground state sublattice magnetizations lie along the crystal $b$ axis, i.e., $\langle S_x \rangle = \langle S_y \rangle = 0$. The first excited state is simply given by $|\epsilon_1\rangle = |0\rangle$.

In this simple model it is assumed, as in the older spin-wave treatments, that the second excited state $|\epsilon_2\rangle$, which corresponds to two-magnon excitations, is irrelevant and that the temperature equals zero. Then the average magnetization is a simple function of the parameter $\alpha$:

$$|\epsilon_2\rangle = |\epsilon_1\rangle$$

and the MF equations (26) can be written analytically as

$$\beta = \arctan \left( \frac{\text{Im}(A_Z)}{\text{Re}(A_Z)} \right)$$

with the constant

$$X = -2 \sqrt{\frac{3}{2}} \left( J(0)_{\text{intra}} - J(0)_{\text{inter}} \right) + \sqrt{\frac{3}{2}} \left[ T_0(0)_{\text{intra}} - T_0(0)_{\text{inter}} \right]$$

and the parameters $A_2, J(0)$, and $T_0(0)$ given by Eqs. (24) and (25). From Eq. (29) $\alpha$ can easily be found self consistently, starting from $\alpha = 0$, whereas $\beta$ is directly given. The MF excitation energy is found to be

$$\Delta \epsilon = \sqrt{2 \left( X^2 \cos^2 \alpha + |A_Z|^2 \right) - X \cos \alpha}$$

The second step in the spin-wave method involves the solution of the RPA equation, cf. Sec. II B. This problem is more complicated than the usual spin-wave problem with the Hamiltonian (11), due to the explicit consideration of the dipole–dipole interaction as a two-body operator and due to the tensorial character of the coupling parameters $A$ and $T_{pp'}$. Still it can be solved analytically and the magnon frequencies are given by

$$\omega_{1,2}(q)^2 = |\Delta \epsilon + Y_{\text{intra}}^2 - Y_{\text{inter}}^2 + Z_{\text{intra}}^2 - Z_{\text{inter}}^2|$$

$$\pm 2 \left( |\Delta \epsilon + Y_{\text{intra}}^2| Z_{\text{inter}} - Y_{\text{inter}} Z_{\text{intra}}^2 \right)^{1/2} - \left( \text{Im} Z_{\text{intra}} Z_{\text{inter}}^2 \right)^{1/2}.$$
The constants $Y$ and $Z$ (both for intra/inter) are fairly complicated combinations:

$$Y = -2J(q) - \frac{1}{\sqrt{30}} T_0(q) - \sin \alpha \Re(e^{-i\theta} T_2(q)),$$

$$Z = e^{i\theta} \left[ 2J(q) \sin \alpha + \frac{1}{\sqrt{30}} T_0(q) \sin \alpha + \frac{1}{\sqrt{5}} \Re(e^{-i\theta} T_2(q)) + i \cos \alpha \Im(e^{-i\theta} T_2(q)) \right]$$

(33)

of the $q$ dependent lattice sums $J(q)$ and $T_m(q)$ defined by Eq. (25).

The lattice sum $J(q)$ is easily calculated. Because of the exponential decay of $J_{pp}$, with the intermolecular distance $r_{pp}$, only the nearest and next-nearest neighbors within the layers parallel to the $a$-$b$ plane and the nearest and next-nearest neighbors in the adjacent layers contribute. The lattice sums $T_m(q)$ over the (magnetic) dipole–dipole interaction converge very slowly when taken in direct space. In order to evaluate these sums we have invoked the $q$ dependent Ewald formula\(^3\) which writes part of the sum in reciprocal space and which leads to rapid convergence. The macroscopic term which occurs\(^3\) for $q = 0$ vanishes for antiferromagnetic lattices. The magnon frequencies obtained by this simple analytical expression (32) can be compared with some of the numerically calculated eigenvalues of the full RPA matrix, Eq. (22), or with the eigenvalues of the pure spin blocks (SS) of this matrix. Thus, the results, which are discussed in Sec. III, inform us about the separability of the lattice dynamics and spin-wave problems and about the validity of the simplified model for the spin waves.

III. RESULTS AND DISCUSSION

A. General remarks

The \textit{ab initio} calculations on the O$_2$–O$_2$ dimer\(^3\) have provided the spin-independent O$_2$–O$_2$ potential $V_{pp}$ and the geometry dependent Heisenberg coupling parameter $J_{pp}$, directly in the form of a spherical expansion as in Eq. (3). For the expansion coefficients we have chosen the following forms:

$$u_{L_{aL_{pp}}}(r_{pp}) = C_{L_{aL_{pp}}}^L \exp(- \alpha_{L_{aL_{pp}}} r_{pp}) - \beta_{L_{aL_{pp}}} r_{pp}^2 + C_{L_{aL_{pp}}}^{\text{mult}} \exp(-L_a + L_p + 1),$$

$$+ C_{L_{aL_{pp}}}^{(6)} r_{pp}^6 + C_{L_{aL_{pp}}}^{(8)} r_{pp}^8 + C_{L_{aL_{pp}}}^{(10)} r_{pp}^{10}$$

and

$$J_{L_{aL_{pp}}}(r_{pp}) = C_{L_{aL_{pp}}}^L \exp(- \alpha_{L_{aL_{pp}}} r_{pp}) - \beta_{L_{aL_{pp}}} r_{pp}^2.$$

(34)

The exponential contribution to Eq. (34) is due to overlap (exchange and charge penetration) effects, the second term is due to the electrostatic multipole interactions and the last three terms arise from dispersion interactions. The expansion coefficients of the Heisenberg coupling parameter, Eq. (35), just contain an exponential term because this coupling is caused merely by exchange effects. All the coefficients occurring in these equations have been explicitly calculated in Ref. 21, except for the $C_{L_{aL_{pp}}}^{(n)}$. Apart from the leading isotropic coefficient $C_{0000}^{(6)}$, good values for these coefficients are not available in the literature either. So we have estimated these parameters $C_{L_{aL_{pp}}}^{(n)}$ via simple model considerations. In order to check whether this uncertainty influences the conclusions, three different sets of parameters $C_{L_{aL_{pp}}}^{(n)}$ have been tested. The first set ($A$) has been obtained by assuming that the O$_2$–O$_2$ dispersion interactions can be represented by a $C_{0000}^{(6)} r^{-6}$ atom–atom potential, which is approximately equal to the potentials used by Kobashi \textit{et al.}\(^3\) and by expanding this atom–atom $r^{-6}$ potential in the form of Eq. (3). Explicit formulas for such expansions have been derived.\(^3\) The second set ($B$) has been obtained by using the same model, but now we have scaled $C_{0000}^{(6)}$ in the atom–atom potential to the value that reproduces the experimental cell parameters in $\alpha$-O$_2$ when the free energy is minimized by isotropic expansion of the lattice. In constructing the third set ($C$) we have started from the accurate semiempirical potential\(^3\) of $C_{0000}^{(6)}$ and taken the anisotropy factors $C_{L_{aL_{pp}}}^{(6)} / C_{0000}^{(6)}$ from \textit{ab initio} calculations.\(^3\) The higher coefficients $C_{L_{aL_{pp}}}^{(n)}$ for $n = 8, 10$ were then related to the coefficients with $n = 6$ by using the same ratios calculated for the N$_2$–N$_2$ potential.\(^3\) Some adjustments of these ratios had to be made, however, in order to obtain a reasonable lattice energy for $\alpha$-O$_2$ and optical librion frequency in $\beta$-O$_2$. All the three sets of parameters $C_{L_{aL_{pp}}}^{(n)}$ are listed in Table I. Together with the parameters given in Ref. 21 and with the $O_2$ bond length and the values of the intra- and intermolecular spin coupling parameters, also given in Table I, these parameters completely specify the spin-dependent O$_2$–O$_2$ potential.

The cell parameters used in our calculations on $\alpha$-O$_2$ and $\beta$-O$_2$ are listed in Table II. It would have been possible to optimize these cell parameters by minimizing the free energy, as we have done for nitrogen.\(^26\) We found this too expensive, however, and not very meaningful because of the uncertainty in the dispersion coefficients.

Next we specify the basis sets used in our (mean-field) calculations. The translational vibrations of the molecules have been expanded in a basis $|Y_m^{(n)}(\omega_p)\rangle$ of three-dimensional harmonic oscillator functions. For the displacement vectors $\mathbf{u}$, we have used polar coordinates, so that the angular parts of the (isotropic) oscillator functions are given by spherical (or in practice, tesseral) harmonics and the radial parts by modified Laguerre functions, see Ref. 26. Convergence of the MF states was reached for $n_{\text{max}} = 3$, but in order to ensure the correct behavior of the acoustic phonon branches in the RPA calculation, we had to include all oscillator functions with $n < n_{\text{max}} = 5$. As explained in Ref. 26, this is related to the translational invariance property of the lattice dynamics formalism, which is satisfied for the RPA method, but only in the limit of a complete basis set. The librational states of the molecules have been expanded in tesseral harmonics, i.e., real combinations of spherical harmonics $|Y_m^{(n)}(\omega_p)\rangle$. For homonuclear O$_2$ molecules, we only need functions with odd $\ell$ because of the zero nuclear spin momentum and the $E_g$ symmetry character of the electronic ground state. Since the librational states of the O$_2$...
molecules in the $\alpha$ and $\beta$ solids are fairly localized, we needed rather many of these free rotor functions for convergence. For $1 \leq l_{max} = 13$ the MF ground state was converged to within 1 cm$^{-1}$, the first two excitation energies to within 2 cm$^{-1}$. The spin basis is simply given by the triplet functions $|S,M_S\rangle$ with $S=1$ and $M_S = -1, 0, and 1$.

It has been explained in Sec. II B that the pair terms in the potential, which depend on the intermolecular distances $r_{pp}$, have to be written as explicit functions of the displacement coordinates $u_p$ and $u_p'$. We have achieved this by means of a double Taylor expansion, including all terms in $u_p^2 u_p'^2$ up to powers $\alpha_1 + \alpha_2 < 4$. The calculations on solid nitrogen,26 where the same method has been used, show that these terms are largely sufficient to take into account all the anharmonicity in the translational vibrations. Let us emphasize at this point that our method is also valid for strongly anharmonic librations with very large amplitudes, because it retains the full orientational dependence of the potential. In some of the calculations, where we focus on the librions and magnons, we have kept the molecular centers of mass fixed on the lattice sites.

### TABLE II. Cell parameters of solid oxygen.

<table>
<thead>
<tr>
<th>$\alpha$-O$_2$:</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>5.403 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$b$</td>
<td>3.429 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>5.086 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>122.33°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\beta$-O$_2$:</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>3.272 Å</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$c$</td>
<td>11.277 Å</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
These results and also those in Table VII are slightly different from those in Ref. 22 because the latter have subscripts refer to (next) nearest neighbors. The Heisenberg exchange parameters (T = 30 K) are listed in Table IV. Only four of such couplings are significant. All coupling parameters are raised in absolute value by the averaging over the translational vibrations, but lowered by librational averaging. The latter effect dominates. The resulting values for the nearest neighbor intersublattice couplings in \( \alpha-O_2 \) and \( \beta-O_2 \) fall well within the range of experimental data quoted in DeFotis's review, but they are less negative than the more recent experimental values. These more negative values are mainly based on magnetic susceptibility data, however, which have only been inter­pretated via MF theory. The ratios \( J_{NN}/J_{NN} = 0.39 \) for \( \alpha-O_2 \) and \( J_{NN}(\beta-O_2)/J_{NN}(\alpha-O_2) = 0.76 \) are in agreement with experimental. The interlayer couplings are small and they become even smaller by librational averaging. This agrees with the experimental data that suggest \( \alpha- \) and \( \beta-O_2 \) to be quasi-two-dimensional magnetic systems, but the sign of our interlayer coupling parameters does not agree with experiment. We expect that the positive sign of the \( ab \text{ initio} \) values for \( J' \) may be incorrect, because the geometry of the interlayer neighbor pairs is close to geometries for which the calculated \( J' \) values change sign. Although our calculated positive \( J' \) would lead to a magnetic ground state of \( \alpha-O_2 \) with reversed spins an alternating layer, we have still based our MF and RPA calculations on the experimentally observed magnetic ground state. The drawback of this discrepancy is that the spin waves in our RPA calculations will become soft for some \( \mathbf{q} \) vectors along the \( c^* \) direction. Since the effect of the weak interlayer coupling on most properties is small indeed, we have, at this stage, not tried to correct this error.

In \( \beta-O_2 \) the interlayer coupling causes still another problem. It has been pointed out by one of us and by others, that the three-sublattice structure which is favored by the antiferromagnetic intralayer exchange coupling will be distorted by the interlayer coupling. So, in the ground state the magnetic structure of \( \beta-O_2 \) will be incommensurate and via the geometry dependence of the Heisenberg coupling terms, the symmetry of the lattice will be distorted too. This would complicate our calculations to a large extent. Since the effects of the interlayer exchange coupling are very small, we have omitted this coupling from our calculations on \( \beta-O_2 \) and based ourselves on the experimentally observed geometry with the antiferromagnetic three-sublattice structure. Also the magnetic dipole-dipole coupling has been left out of our spin-wave calculations on \( \beta-O_2 \), and both anisotropic spin terms have been left out of the lattice dynamics calculations since they would lead to similar problems.

By calculating the Helmholtz free energy both for \( \alpha- \) and \( \beta-oxygen \) as a function of the temperature, we have investigated whether the spin-dependent potential correctly predicts the \( \alpha-\beta \) transition. It is indeed found, as shown in Fig. 2, that the \( \alpha \) phase is more stable at low temperature and

### TABLE III. Translational and librational amplitudes from MF calculations (potential C).

<table>
<thead>
<tr>
<th>( \alpha-O_2 )</th>
<th>( T = 0 \text{ K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (u_\alpha^2)^{1/2} )</td>
<td>0.1092 Å</td>
</tr>
<tr>
<td>( (u_\beta^2)^{1/2} )</td>
<td>0.1115 Å</td>
</tr>
<tr>
<td>( (u_\gamma^2)^{1/2} )</td>
<td>0.0889 Å</td>
</tr>
<tr>
<td>( \arccos((\cos^2 \theta)^{1/2}) )</td>
<td>10.84°</td>
</tr>
<tr>
<td>Asymmetry parameter</td>
<td>( \frac{(\sin^2 \theta (\sin^2 \phi - \cos^2 \phi))}{(\sin \theta)} )</td>
</tr>
</tbody>
</table>

### TABLE IV. Effective exchange coupling parameters (in K), calculated with potential C.

<table>
<thead>
<tr>
<th>( \alpha-O_2 )</th>
<th>( T = 0 \text{ K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{NN} )</td>
<td>-12.677</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-5.164</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.538</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.368</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-9.561</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-0.002</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.487</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( \beta-O_2 )</th>
<th>( T = 30 \text{ K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( J_{NN} )</td>
<td>-10.133</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-3.858</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.352</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.274</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-11.120</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>-0.001</td>
</tr>
<tr>
<td>( J_{NN} )</td>
<td>0.322</td>
</tr>
</tbody>
</table>

The Heisenberg exchange parameters \( J \) and \( J' \) refer to the intra- and interlayer couplings, respectively; the subscripts refer to (next) nearest neighbors.

*These results and also those in Table VII are slightly different from those in Ref. 22 because the latter have been calculated with potential \( B \).
the \( \beta \) phase at higher temperature. The calculated transition temperature, 45 K, (experimentally 23.9 K) is too high, however. But, as one can observe in Fig. 2, the intersection of the two free energy curves is fairly hard to determine. Since we have not varied the lattice parameters and in view of the uncertainty in the dispersion terms of our potential, the error in \( T_{\text{mag}} \) is not surprising. These dispersion terms are spin-independent and not very anisotropic, so they will play little role in most of the properties discussed in the next section. They are important for the lattice stability, however, and thus for the \( \alpha - \beta \) transition temperature. Also the free energy calculated for \( \alpha - \beta \) at \( T = 0 \) K, 10.67 kJ/mol, is in reasonable but not perfect agreement with the experimental\(^{15} \) cohesion energy of 8.66 kJ/mol.

### C. RPA results

Some results from the integrated lattice dynamics and spin-wave calculations are shown in Table V. The magnetic

<table>
<thead>
<tr>
<th>( \omega ) (cm(^{-1}))</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>magnon, &lt; 0.1% libron</td>
</tr>
<tr>
<td>22.1</td>
<td>99.7% magnon, 0.3% libron</td>
</tr>
<tr>
<td>39.3</td>
<td>99.2% libron, 0.8% magnon (( B_x ))</td>
</tr>
<tr>
<td>49.8(^a)</td>
<td>pure phonon</td>
</tr>
<tr>
<td>55.3(^a)</td>
<td>pure phonon</td>
</tr>
<tr>
<td>70.0</td>
<td>libron, &lt; 0.1% magnon</td>
</tr>
<tr>
<td>74.1</td>
<td>libron, &lt; 0.1% magnon (( A_x ))</td>
</tr>
<tr>
<td>86.8(^a)</td>
<td>pure phonon</td>
</tr>
<tr>
<td>101.3</td>
<td>magnon, &lt; 0.1% libron</td>
</tr>
<tr>
<td>101.5</td>
<td>magnon, &lt; 0.1% libron</td>
</tr>
<tr>
<td>124.4(^a)</td>
<td>libron, &lt; 0.1% magnon</td>
</tr>
</tbody>
</table>

\(^a\)These modes correspond to modes at \( q = (0, 2\pi/6, 0) \) in the Brillouin zone of the structural lattice.

![Figure 2](image.png)

**Fig. 2.** Free energy (at zero pressure) for \( \alpha \) and \( \beta \) oxygen, from MF calculations with potential C.

![Figure 3](image.png)

**Fig. 3.** Calculated (RPA) dispersion curves for \( \alpha - \beta \), for phonon (\( T \)), libron (\( L \)), and magnon (\( S \)) modes propagating along the \( b \) axis. Note the avoided crossing and the interchange of \( T/L \) character between two phonon–libron branches at \( q_b \sim 0.45 \).

The lower magnon frequencies in Table V may be compared with the results from the simple analytical spin-wave treatment presented in Sec. II C. The latter results are shown in Table VII, first column. The agreement is very good in—
A. P. J. Jansen and A. van der Avoird: α and β-O₂

pure magnon phonon, <0.1% libron

Character

TABLE VI. Phonon, libron, and magnon frequencies at q = 0 in β-O₂ (potential C).

<table>
<thead>
<tr>
<th>ω (cm⁻¹)</th>
<th>Degeneracy</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1</td>
<td>pure magnon</td>
</tr>
<tr>
<td>15.0</td>
<td>2</td>
<td>pure magnon</td>
</tr>
<tr>
<td>39.5*</td>
<td>2</td>
<td>phonon, &lt;0.1% libron</td>
</tr>
<tr>
<td>53.4*</td>
<td>2</td>
<td>99.8% phonon, 0.2% libron</td>
</tr>
<tr>
<td>54.3</td>
<td>2</td>
<td>pure libron (E₂)</td>
</tr>
<tr>
<td>70.8*</td>
<td>2</td>
<td>93.4% phonon, 6.6% libron</td>
</tr>
<tr>
<td>71.7</td>
<td>1</td>
<td>pure magnon</td>
</tr>
<tr>
<td>71.8</td>
<td>2</td>
<td>pure magnon</td>
</tr>
<tr>
<td>96.4*</td>
<td>2</td>
<td>99.8% libron, 0.2% phonon</td>
</tr>
<tr>
<td>96.4*</td>
<td>2</td>
<td>92.7% libron, 7.3% phonon</td>
</tr>
</tbody>
</table>

The modes correspond to modes at q = 2π/9a (1, √3, 0) and q = 2π/9a (1, −√3, 0) in the Brillouin zone of the structural lattice.

FIG. 4. (a) Percentage of libron character of the two libron-phonon branches that show an avoided crossing in Fig. 3. (b) Percentage of libron character of the two upper libron-magnon branches in Fig. 3, that become degenerate at qb/π = 1.

deed; given the negligible amount of mixing between the magnons and the lattice modes at q = 0 this could be expected. The agreement with the measured magnon frequencies is also very satisfactory, especially if one considers that none of the parameters in our spin-dependent Hamiltonian have been fitted. The different dispersion coefficients chosen in the spin-independent potential, see Table I, practically do not affect the magnon frequencies.

In order to compare our first principles spin Hamiltonian (9) with the phenomenological one, Eq. (1), we have also made spin-wave calculations on α-O₂ with the latter. We have set the Heisenberg parameters Jₚₚ, equal to the calculated values, see Table IV. For the first anisotropy parameter we have taken the free molecule value, A = 5.712 K, and for the second parameter we have adopted the value B = 0.26 K that yields the same spin-anisotropy field as a classical dipole model. The results are listed in the second column of Table VII. The higher magnon frequency, which is mostly determined by the values of J and A is almost the same as for the spin Hamiltonian (9). In the latter Hamiltonian the coupling parameter A has been multiplied by a second rank tensor, see Eq. (6), whose components have to be averaged over the librational states of the molecules, see Eq. (24). The anisotropy component along the x axis (the crystal e* axis) is still 95% of the free molecule value, however, and the components in the ab plane are smaller than 1%. This explains the observed similarity. The lower magnon frequency, which is mainly determined by J and B, is rather different for the spin Hamiltonians (1) and (9). We conclude that it is not justified to replace the exact magnetic dipole–dipole interaction operator in Eq. (9) by an effective single-molecule term in Eq. (1).

Let us now discuss the lattice modes in α- and β-oxygen, especially the two libron modes that correspond with q = 0 in the structural unit cell. These modes have been observed by Raman spectroscopy in the monoclinic β phase they are degenerate with E₈ symmetry, at a frequency of 48 cm⁻¹. In the monoclinic α phase the a and b axes are no longer equivalent and, in principle, one finds two branches, one with B₈ symmetry for the librations about the crystal a axis and one with A₄ symmetry for librations about the b axis. The splitting between the two Raman peaks observed (at 42 and 74 cm⁻¹) for α-O₂ is very large, however, in view of the small structural distortion. Lattice dynamics calculations have never yielded a splitting more than 10 cm⁻¹. Therefore, it has mostly been assumed that the A₄ and B₈ modes remain accidentally degenerate at about 42 cm⁻¹ and that the higher frequency mode should be interpreted as a two phonon/libron or libron–magnon transition. In support of this explanation, it has been suggested by Kuchta on the basis of model calculations that the Heisenberg exchange term would help in restoring the A₄–B₈ degeneracy. Ettets et al. have proposed that the higher frequency belongs to a libron mode which lies at the edge of the Brillouin zone for the structural lattice, but which has q = 0 in the magnetic Brillouin zone. This mode could become visible in Raman spectroscopy when there is a strong coupling between the librions and the spins. The weakest point of all these interpretations is, however, that under various temperatures and pressures no indication of the doublet character of the lowest peak in α-O₂ has been observed. Recent temperature dependent Raman measurements suggest that the lower frequency peak corresponds with the B₈ mode and the higher one with the A₄ mode, so that the splitting would be about 32 cm⁻¹ indeed.

Our calculations offer a clear explanation of this problem. It can be observed in Table VIII that, for any of the three potentials that we have taken the splitting between the B₈ and A₄ libron modes lies between 30 and 40 cm⁻¹. Most of the splitting disappears if the Heisenberg term is omitted from the calculations. Therefore, the older lattice dynamics calculations which have not included this term or included it via a simple empirical model, have failed to find this splitting. It is only by the extremely strong anisotropy of the Heisenberg coupling parameter J, which has been found from the ab initio calculations, that the large splitting is correctly reproduced. This is confirmed by the plot of the lattice potential in Fig. 5 along the normal coordinates for the B₈ and A₄ librions, with and without the contribution of the Heisenberg term. We observe that this term lowers the
TABLE VII. Optical (q = 0) magnon frequencies in $\alpha$-O$_2$ (potential C).

<table>
<thead>
<tr>
<th></th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>First principles from Eq. (9)</td>
</tr>
<tr>
<td>$\omega$(cm$^{-1}$)</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>22.2</td>
</tr>
</tbody>
</table>

lattice energy of $\alpha$-O$_2$ at the equilibrium geometry. At the same time it drastically increases the stiffness of the potential in the $A_g$ direction, but much less in the $B_g$ direction. Actually this was clearly visible already in Fig. 2 of Ref. 21.

The calculations with the different potentials $A$, $B$, and $C$ also yield the correct relative magnitudes of the $B_g$ and $A_g$ libron frequencies in $\alpha$-O$_2$ with respect to the $E_g$ frequency in $\beta$-O$_2$. In any case, the inclusion of the Heisenberg term appeared to be essential. The values of the frequencies are best reproduced by potential $C$, which has been partly adjusted to the $E_g$ frequency in $\beta$-O$_2$.

IV. CONCLUSIONS

We have proposed a lattice and spin Hamiltonian for solid O$_2$ with a form that is completely derived from first principles, and we have developed an integrated lattice dynamics and spin-wave formalism that can be used with this Hamiltonian. Apart from the kinetic energy and the spin-independent intermolecular potential, which are present in any molecular crystal, the Hamiltonian describes the coupling between the O$_2$ triplet spin momenta. The first of the spin-coupling terms is the usual Heisenberg exchange term, which is isotropic in spin space, the second one is due to the intramolecular spin–orbit and spin–spin coupling and the third term describes the magnetic dipole–dipole interaction as a two-body spin operator. The spin factor $(S_p \cdot S_p)$ changes from $\sim -1$ for the nearest neighbors in $\alpha$-O$_2$ to $\sim -0.5$ for those in $\beta$-O$_2$, which yields a discontinuity in the anisotropic potential at the $\alpha$–$\beta$ phase transition. The coupling parameters in our spin hamiltonian have been obtained by averaging (renormalizing) the $ab$ initio parameter functions over the lattice vibrations. So, in contrast with the earlier spin-wave treatments, we were not obliged to fit any empirical parameters. Another essential improvement upon these treatments is the explicit consideration of the magnetic dipole–dipole interaction as a two-body spin operator. The only non $ab$ initio data in our approach are the long range dispersion coefficients in the spin-independent potential. By choosing different values for these coefficients we have demonstrated, however, that our conclusions do not depend on this choice.

The optical (q = 0) magnon frequencies from the spin wave calculations on $\alpha$-O$_2$ are in fair agreement with the values from infrared and Raman spectrometry. Especially if one considers that no parameter fitting was involved in these

<table>
<thead>
<tr>
<th>Potential</th>
<th>Putting $J = 0$</th>
<th>Including $J(r_{pp} \cdot \omega J(p \cdot \partial J_p))$</th>
<th>Experiment Ref. 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-O$_2$: $B_g$</td>
<td>23.9</td>
<td>19.7</td>
<td>38.9</td>
</tr>
<tr>
<td>$A_g$</td>
<td>37.8</td>
<td>34.7</td>
<td>50.7</td>
</tr>
<tr>
<td>$\beta$-O$_2$: $E_g$</td>
<td>28.4</td>
<td>24.6</td>
<td>42.9</td>
</tr>
</tbody>
</table>
calculations, this is very satisfactory and it supports the validity of our first principles Hamiltonian. A more detailed study of the magnetic properties of solid O\textsubscript{2} will be described in a subsequent paper.\textsuperscript{46}

The lattice dynamics results are even more rewarding. They have led to a unique assignment of the Raman (\(q = 0\)) libron peaks in \(\alpha\)- and \(\beta\)-O\textsubscript{2}. The large splitting between the peaks in \(\alpha\)-O\textsubscript{2}, which could not be explained by any of the previous lattice dynamics calculations, appears to be caused by the extremely strong anisotropy of the Heisenberg exchange coupling parameter. For this reason, it was crucial to include the Heisenberg term in the lattice dynamics calculations and to know its dependence on the molecular orientations from \textit{ab initio} calculations.

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